REMARKS

Claims 1, 2, 4, 5, 7, and 9-11 remain pending in this application. Claims 6 and 8 have been canceled without prejudice or disclaimer. Claim 1 has been amended to add the recitations of claims 6 and 8, and to recite that the crystallinity of the fine fibers is 15-40% as described in the present specification at, for example, page 8, lines 19-22. Claims 5 and 7 have been amended to cure the insufficient antecedent basis. No new matter has been introduced by these amendments.

Rejection Under 35 U.S.C. § 112, Second Paragraph

Claim 5 has been rejected under 35 U.S.C. § 112, second paragraph as being indefinite, for failing to particularly point out and distinctly claim the subject matter that Applicants regard as their invention. Office Action at 2. The Office bases the rejection on Claim 5 having insufficient antecedent basis for the limitation "continuous filamentary fibers." Applicants have amended Claim 5 in order to more clearly define the invention by using the language of Claim 1, from which Claim 5 depends. Accordingly this rejection should be withdrawn.

Rejection Under 35 U.S.C. § 103(a)

Claims 1-2 and 4-11 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over Perkins et al., U.S. Patent No. 5,178,932. The Office argues that Perkins teaches a multilayered laminate comprising an inner meltblown layer having a diameter of 0.1-10 micrometers and two outer layers comprising fibers having a diameter in excess of 7 micrometers, and teaches that the interfaces between the layers are significantly intermingled.

As to claims 1 and 9, and claims dependent thereon, Perkins does not in any way suggest the fine fibers having a crystallinity ranging from 15% to 40%, as recited in

-5-

claims 1 and 9 and all claims dependent thereon. Furthermore, the Office neither explains how Perkins discloses a crystallinity, or how it would be obvious to one of ordinary skill in the art reading Perkins to use a fine fiber with the crystallinity as instantly claimed.

Perkins does not teach or otherwise provide any reason to observe this crystallinity in the fine fiber thermoplastic resins disclosed therein, or appreciate its importance in achieving the recited intrusion index. As noted at page 14, lines 26-36 and at page 15, lines 1-6 of the present specification, fine fiber crystallinity higher than 40% contributes to a lower bonding strength between the fine fibers and the filamentary fibers which causes a decrease in the intrusion index. A laminated fabric with an intrusion index according to the present invention has a number of favorable characteristics and advantages as described in the specification at page 9, line 29 to page 10, line 6 and the Examples, for example. Also, as noted at page 14, line 26 to page 15, line 6 of the present specification, fine fiber crystallinity lower than 15% contributes to the fine fibers bleeding out from the filamentary fiber layer, adhering to the thermocompressive bonding rolls, becoming a molten lump, or bonding to the rolls and hindering stabilized production of the laminated nonwoven fabric. A person skilled in the art would not find in Perkins any useful information regarding using a fine fiber with a crystallinity within the range as instantly claimed, and the Office has not provided any explanation how it would have been obvious to one of ordinary skill in the art to use a fine fiber with a crystallinity within the instantly claimed range from the teachings of Perkins. For at least this reason, the prior art fails to establish a prima facie case of obviousness.

In addition, the instantly claimed crystallinity would not have been obvious to one of ordinary skill in the art from Perkins' teachings of fine fibers to be used. Perkins teaches using fine fibers chosen from polyolefins, polyesters, polyetheresters, and polyamides. However, as polymers can have a wide range of degrees of crystallinity, which can be dependent upon processing conditions,[1] Perkins' teaching of types of fine fibers to use, does not inherently teach a crystallinity within the claimed range. Commercial polyolefins, for example, which are a preferred embodiment of Perkins, generally have degrees of crystallinity above 50%. *See* present specification, page 23, lines 4-8 and Raghavendra R. Hegde, et al., Olefin Fiber (April 2004), http://web.utk.edu/~mse/Textiles/Olefin%20fibers.htm. Therefore, Perkins teaches the use of fine fibers outside of the range as instantly claimed. Additionally, Perkins provides one of ordinary skill with a practically unlimited number of possible fine fiber crystallinities to choose from, each with varying degrees of crystallinity, and provides no suggestion or reason to 1) use a fiber with a crystallinity within the instantly claimed range, 2) modify a fiber to obtain a crystallinity within the instantly claimed range, or 3) know that crystallinity is a factor to consider when choosing a fine fiber. Accordingly, as Perkins fails to establish a prima facie case of obviousness, this rejection should be withdrawn as to claims 1-2 and 4-11

Furthermore, Perkins does not in any way suggest the fine fibers having the solution viscosity as recited in claims 1, 10, and 11, and all claims dependent thereon. The Office takes the position that although the prior art does not explicitly teach the use

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[1] *See* page 22, line 34 to page 23, line 4 of present specification; *See also* James A. Jacobs & Thomas F. Kilduff, Engineering Materials Technology, 312-324, reproduced at http://mst-online.nsu.edu/mst/polymer/polymer3.htm

of fine fibers having the instantly claimed solution viscosity, it would have been obvious to one of ordinary skill in the art, because Perkins teaches the same types and diameters of fibers in fabrics of the claimed basis weight, combined in the same manner as instantly claimed, to have selected the recited solution viscosity through the process of routine experimentation.

Perkins does not teach or otherwise provide any reason to observe this solution viscosity in the fine fiber thermoplastic resins disclosed therein, or appreciate its importance in achieving the recited crystallinity. As noted at page 22, line 34 to page 23, line 4 of present specification, one aspect in being able to adjust the crystallinity of a fine fiber of polyester resin or polyamide so that it falls within the instantly claimed range, is the fine fiber's solution viscosity. Perkins does not address a solution viscosity, and there is no basis to conclude that the prior art fine fibers would have a solution viscosity within the claimed range. As Perkins also does not address crystallinity, one of ordinary skill in the art would have no reason to use a fine fiber with a solution viscosity within the instantly claimed range, as Perkins does not disclose or suggest the relationship between solution viscosity and crystallinity, and provides no reason for one of ordinary skill in the art to perform routine experimentation to select a solution viscosity. Accordingly, as Perkins fails to establish a prima facie case of obviousness, this rejection should be withdrawn as to claims 1, 2, 4-8, and 10-11.

The Office further takes the position that although the prior art does not explicitly describe the recited characteristics of intrusion index and bulk density, it would have been obvious to one of ordinary skill in the art, because Perkins teaches the same types and diameters of fibers in fabrics of the claimed basis weight, combined in the same

manner as instantly claimed, to have selected these characteristics through the process of routine experimentation. The prior art teachings do not address an intrusion index or bulk density, and there is no basis to conclude that the prior art laminates would have these characteristics within the value ranges recited in claims 1 and 9, and claims dependent thereon, particularly since the prior art does not teach the desirability of using fine fibers having a crystallinity within the range as recited in claims 1 and 9.

While it may be an accurate legal principle that it is generally obvious to determine an optimum value for a result effective variable in a known process, there is no teaching or suggestion in the prior art that intrusion index and bulk density are result effective variables. Accordingly, as Perkins fails to establish a prima facie case of obviousness, this rejection should be withdrawn as to claims 1, 2 and 4-8.

Claims 9-11 are directed to a method of producing a high tenacity nonwoven fabric that is distinguished from the applied prior art by reciting characteristics of the fibers used (e.g., crystallinity from 15 to 40% and solution viscosity) and operating parameters of the thermocompressive bonding step (e.g., temperature and pressure) that are not taught or suggested by the prior art. Although these conditions may be choices individually available to persons skilled in the art, there is no reason for a person skilled in the art to combine them in the way that are recited in these claims. As the prior art fails to establish a prima facie case of obviousness, this rejection should be withdrawn as to claims 9-11.

Prompt and favorable reconsideration is requested.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: November 17, 2008   By: _Charles E Van Horn_

Charles E. Van Horn
Reg. No. 40,266

OLEFIN FIBER

**Updated: April, 2004- Raghavendra R. Hegde, Atul Dahiya, M. G. Kamath,
(Haoming Rong & Monika Kannadaguli)**

1. INTRODUCTION

Olefin fiber is a manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of ethylene, propylene, or other olefin units. Olefin fiber is a generic description that covers thermoplastic fibers derived from olefins, predominately aliphatic hydrocarbons. Olefins are products of the polymerization of propylene and ethylene gases. Polypropylene (PP) and polyethylene (PE) are the two most common members of the family. Polypropylene is extremely versatile as a fiber-forming material, whereas polyethylene is not as good a fiber-forming high polymer material. Since its introduction into the textile industry in the 1950s, the list of successful products and markets for polypropylene fiber has increased exponentially [1]. Figure 1 shows the forecasted world consumption of nonwovens in millions of tons from 1998 to 2007[2].

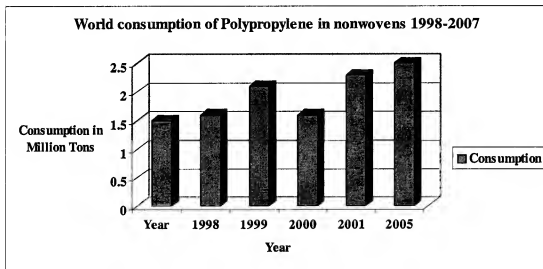**World consumption of Polypropylene in nonwovens 1998-2007**

Fig 1 Forecasted world consumption of Polypropylene in Nonwovens in Millions of Tons till 1996-2007 [2]

Of the polypropylene used in the U.S., more than one-third goes into fiber and fiber-related products. The declining price and continuing improvements in the quality of polypropylene resins, plus the low specific gravity of the polymer (which provides high covering power), have been important factors in the development of new product end uses.

2. PRODUCTION TECHNOLOGY FOR POLYOLEFINS

2.1 HIGH PRESSURE PROCESS FOR BRANCHED LDPE

- Autoclave reactor process
- Tubular reactor process

2.2 POLYMERIZATION PROCESS FOR LINEAR HDPE, MDPE, LLDPE AND COPOLYMERS

- High-pressure autoclave reactor
- Low-pressure liquid slurry processes
- Low and medium pressure solution processes
- Low pressure gas phase processes

2.3 POLYMERIZATION PROCESS FOR PP AND PROPYLENE COPOLYMERS

All the above processes have been used in the production of PP. The special process Technologies for PP and propylene copolymers include two kinds of liquid pool slurry Process:

- Low pressure liquid pool slurry phase processes
- Low pressure modular gas phase reactory

2.3 POLYMERIZATION PROCESS OF OTHER POLYOLEFINS

- Slurry phase heavy-diluents stirred-tank reactor
- Slurry phase light-diluents stirred-tank reactor
- Tubular high-pressure process
- Solution phase medium-pressure adiabatic reactor

3. PROCESSING METHODS OF POLYOLEFINS

There are six important processing methods for Polyolefins, these are:

- Injection molding
- Rotational molding
- Blow molding
- Extrusion
- Blown film extrusion
- Cast film extrusion

3.1 PROCESSABILITY OF POLYPROPYLENE (PP)

A major virtue of polypropylene is its ability to be used in a wide range of fibrous forms[3]. Fibrous forms of polypropylene include staple, bicomponent staple, monofilament, multifilament, slit film yarns, slit-fibrillated film yarns, spunbonds, melt blown nonwovens, synthetic pulps, and extruded nettings. It can be made into ropes and cordage, primary and secondary carpet backing, carpet face yarns, upholstery fabrics, geotextiles, filtration materials, horticulture/agriculture materials, automotive fabrics, spill-cleanup materials, disposable diapers, hospital/medical care materials, and protective clothing. The melting point of polypropylene (160-170°C) is an advantage in many nonwovens processing steps. PP fiber can be softened sufficiently to bond to one another without destroying fiber properties. Nonwoven fibers made from polypropylene can therefore be fusion-bonded, eliminating the need for chemical binders. The benefits of this technique include both energy saving and environmentally friendliness. Uses of thermally bonded cover stock in baby diapers and similar products will result in a markedly increased use of polypropylene. The fusion characteristics of polypropylene are used not only to bond carded webs but also to improve the dimensional stability of needle-bonded fabrics. A large amount of engineered fabrics for road stabilization, dam and lake reinforcement, soil stabilization and roofing are made from polypropylene fibers. Melt-blown fabrics are widely used in filtration media, battery separators, etc. The relatively high melting point allows PP nonwovens to be used up to the temperature of 120°C before softening occurs. The soft hand and hydrophobic properties make PP nonwovens particularly suitable for hygiene products, baby diapers and adult incontinents. Spunbond and meltblown

are the two main processes for polypropylene nonwoven fabrication. Both techniques require PP resins with high melting flow rate and relatively very narrow molecular weight distribution. The fibers produced in spunbonded nonwovens are spun filaments, whose diameters are in the range of 10-35 microns, whereas the fibers of meltblown nonwovens are usually discontinuous and much finer, typically less than 10 microns. This partially explains why meltblown webs are usually weaker than spunbonded webs. Processability of a polymer is highly dependent on its rheological properties, which have close relationship with its molecular weight, molecular weight distribution, and temperature and shear rate. PP resins are generally categorized according to their melt flow rates (MFR), which is the amount of material that passes through a standard die hole for ten minutes. Polymers with higher molecular weight have lower MFR and higher viscosity (under a given temperature). Commercial polypropylene has a wide range of MFR from 0.25 to 1200. MFR is a very important parameter for both melt-blown and spunbond processing. PP melts exhibit non-Newtonian viscosity, normal stress in shear flow, excessive entrance and exit pressure drop, die swell, melt fracture and draw resonance. PP melts are more viscoelastic than PET and nylon melts. The flow pattern and stability of PP melts are highly dependent on the shear rate. Above the critical shear rate, melt fracture may occur.
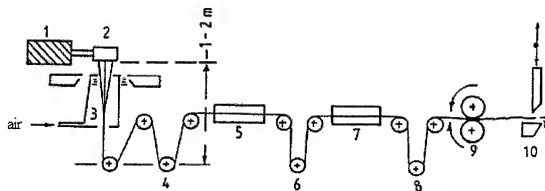
Processability of polypropylene fiber is also influenced by the die geometry. The L/D ratio has to be optimized to reduce instability and the effects of PP's high viscosity. Both melt fracture and draw resonance represent instabilities in flow. Draw resonance is a periodic variation in diameter of a spinning threadline above a critical draw-down ratio. Slowing down the drawing operation or a suitable cooling procedure may prevent this. In addition, processability of polypropylene fiber can also be affected by other factors such as finishing. Finish oil is a mixture of several chemicals that function as anti-static agent and lubricator to protect the filament. The results of the effects of finishing on this area are not available in this report yet. Since unmodified polypropylene is not dyeable, pigmentation has become the preferred way of coloration in textile and textile-related applications. Generally, the fastness properties of pigmented fibers are superior to those of dyed fibers. Pigmented polypropylene fibers have become established for contract carpets, indoor/outdoor carpeting, synthetic turf, and other applications, in part because of their superior fastness properties. Light stabilizers have helped to open new markets for products intended for use outdoors, and improved heat stabilizers have boosted extrusion efficiency and allowed use of more recycled material.

4. CHARACTERISTICS OF OLEFIN FIBERS

- Good bulk and cover, very lightweight (olefin fibers have the lowest specific gravity of all fibers)
- High strength (wet or dry)
- Resistant to deterioration from chemicals, mildew, insects, perspiration, rot and weather
- Abrasion resistant
- Low moisture absorption
- Stain and soil resistant
- Lowest static component of any man-made fiber
- Sunlight resistant
- Good washability, quick drying, unique wicking
- Resilient, moldable, very comfortable
- Thermally bondable

5. MANUFACTURE OF PP FIBER/FILAMENT

Polypropylene chips can be converted to fiber/filament by traditional melt spinning, though the operating parameters need to be adjusted depending on the final products. Spunbonded and melt blown processes are also very important fiber producing techniques for nonwovens. As an example, the staple fiber production is shown in Fig. 2.

1-extruder, 2-Spinning pack, 3-Quench duct.4.6.8-Drawing.Tensioning,

5-Hot streching,7-stabilizing,9-Crimper 10-cutter

Fig.2: Schematic diagram of staple fiber production unit of PP.

Identifiers are shown with the figure. Additional comments and description are as follows:

1. Extrusion: L/D=30, compression ratio=1:3.5
2. Metering: one or more spinning gear pumps receives the molten polymer and sends it through the spinning pack to homogenize the product, feed the spinning pack at a constant rate, and prevent fluctuation due to screw extruder.
3. Spinning: the spinning pack consists of three parts-filters, distributor (which distributes the molten polymer over to die surface) and the die. The diameter of the die varies from 0.5 to 1.5mm, depending on the denier required.
4. Quenching: newly extruded filaments are cooled in a good " box" which will distribute 3 m³/min of cool air without damaging the filaments.
5. Finishing: to improve antistatic and reduce abrasion.
6. Hot Stretching: to enhance the physico-mechanical properties.
7. Crimping: to improve the bulk.
8. Thermosetting: it is a treatment in hot air or steam that removes the internal stresses and relaxes fibers. The resultant fibers are heat-set with increased denier.
9. Cutting: fibers are cut into 20 to 120 mm length depending on whether they are intended for cotton or woolen system.

For more information about melt spinning processing, reference 3 is recommended. The spunbonded and melt blown techniques will be described in the following chapters.

6. PROPERTIES OF PP FIBER

6.1 FIBER STRUCTURE

Polypropylene fibers are composed of crystalline and non-crystalline regions. The spherulites developed from a nucleus can range in size from fractions of a micrometer to centimeters in diameter. The a-axis of the crystal unit cell is aligned radially and the chain axis is homogeneously distributed in planes perpendicular to this radial direction. Each crystal is surrounded by non-crystalline material. Fiber spinning and drawing may cause the orientation of both crystalline and amorphous regions. If the

extension is less than 0.5%, the spherulite deformation is elastic and no disruption of the structure occurs, otherwise spherulites are highly oriented in the direction of the force and finally are converted to microfibrils. These highly anisotropic microfibrillar structures lead to anisotropic fiber properties.

6.2. CRYSTALLINITY OF PP FIBER

The degree of crystallinity of PP fiber is generally between 50-65%, depending on processing conditions. Crystallization occurs between glass transition temperature (Tg) and the equilibrium melting point (Tm). The crystallization rate of PP is fast at low temperature. It is reported [5] that the crystallization rate decreases with increasing crystallization temperatures and also decreases with the increase of molecular weight as shown in Fig 3. A paracrystalline structure with only 45% crystallinity resulting from immediate quenching after extrusion was observed. A significantly higher crystallinity of 62% was achieved when quenching further downstream of the die. Although the drawing orients the crystallites, it also might decrease the crystallinity as shown in Fig 4[5], which is different from that of PET and PAN fibers.
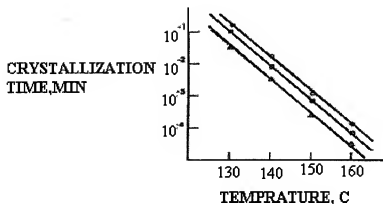

Fig. 3: Relationship between rate of crystallization and temperature for PP of various molecular weights [4].
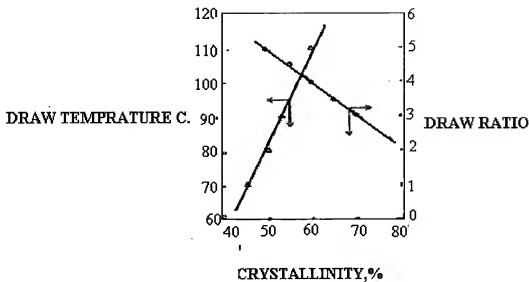
Fig.4: Effect of draw ratio and draw temperature on PP-fiber crystallinity: at draw temperature of 100° C; Δdraw ratio of 4:1[4]

The crystalline structure of PP has different forms, subject to its respective drawing condition, as shown in Fig 5. For example, the "alpha-form" is thermodynamically more stable and accordingly requires greater drawing force than the other two.
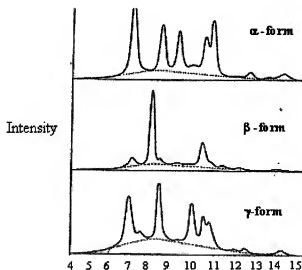

Fig 5: Crystalline structure of PP fibers

Heat setting removes the residual strains and produces a defect-free and stable crystalline structure to make fiber/fabrics dimensionally stable. It also improves the percentage of overall crystallinity. The smectic structure changes to a more perfect monoclinic structure. During the process of heat setting if the temperature is above 70°C. At 145°C the conversion is almost complete. In comparison to the predominantly smectic form, the monoclinic form does not experience any major change in crystalline

structure during the course of drawing and heat setting.

6.3. MECHANICAL PROPERTIES

The general physical properties of PP fibers are shown in Table 1. Polypropylene fibers are produced in a variety of types with different tenacities designed to suit varying market requirements. Fibers for general textile uses have tenacities in the range of 4.5-6.0 g/den. High tenacity yarns up to 9.0 g/den are produced for the use in ropes, nets and other similar applications. High performance PP fibers have been made with high strength and high modulus. The techniques include ultra-drawing[6], solid-state extrusion[7] and crystal surface growth[8]. The filaments with tenacities over 13.0 g/den can be made.

Table 1: Physical properties of Polypropylene

Moisture Regain	< 0.1%
Refractive Index	1.49
Thermal Conductivity	0.95Btu-in/ft^2 .hr.°F
Coefficient of linear thermal expansion	4.0x10^{-5}/°F
Heat of fusion	21 cal/g
Specific heat	0.46 cal/g.c
Density of Melt at 180°c	0.769 g/cc
Heat of Combustion	19,400 Btu/lb
Oxygen index	17.4
Decomposition temperature range	328-410°C
Dielectric constant (0.1 MHz)	2.25
Dissipation factor (0.1 MHz)	< 0.0002
Specific volume resistively	> 10^{16} Ω. Cm

The degree of orientation achieved by drawing influences the mechanical properties of PP filaments. The greater the degree of stretch, the higher the tensile strength and the lower the elongation as shown in Fig. 6. Commercial PP monofilaments have an elongation-at-break in the range of 12-25%. Multifilaments and staple fibers are in the range of 20-30% and 20-35%, respectively.
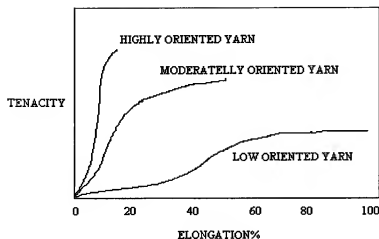
Fig.6: Relationship between mechanical property and stretching of PP fibers [11]

6.4. THERMAL PROPERTIES

Polypropylene fibers have a softening point in the region of 150°C and a melting point at 160-170°C. At temperatures of -70°C or lower, PP fibers retain their excellent flexibility. At higher temperature (but below 120°C) PP fibers nearly remain their normal mechanical properties. PP fibers have the lowest thermal conductivity of all commercial fibers. In this respect, it is the warmest fiber of all. The thermal conductivity of common textile fibers is shown in Table 2.

Table 2: Thermal Conductivity of textile fibers

Material	Thermal Conductivity
Air	1.0
PP	6.0
Wool	6.4
Acetate	8.6
Viscose	11
Cotton	17.0

6.5. DYEABILITY

The dyeability of fibers is controlled by both chemical and physical properties. Fibers that have polar functional groups in their molecular repeat units can more easily be dyed. These polar groups may serve as active sites for combination with dye molecules by chemical bonds. Since PP molecular chains have no polar functional groups, the dye molecules cannot be chemically attracted to the fibers. The dye molecules cannot even be strongly adsorbed by the fiber surfaces because of their hydrophobic properties. Therefore, these adsorbed molecules, which interact with the fiber surface by weak van der Waal's force, are easily washed away. In addition, PP fiber has relatively high crystallinity (50-65%),

which partially attributes to its very low dyeability.

Fiber modifications have been investigated to make polypropylene dyeable this includes copolymerization to provide dyesites along the macromolecular chain and blend with dyeable polymers. Baumann [9] has reviewed the attempts by several researchers to improve polypropylene dyeability. The method of grafting chloromethylstyrene has been introduced. In addition, the method of blending a polyethyleneimine compound with polypropylene was described briefly. Bromination of polypropylene fibers was reported to give PP fibers an affinity for basic dyes [10]. These methods have, owever, generally led to the significant decrease of the desirable physical properties of polypropylene fibers.

In recent years, surface modification of hydrophobic fibers by plasma treatment has opened up new possibilities in this field. Functional groups can be introduced onto the surface of PP fibers by special gas plasma treatment or plasma polymerization [11]. The polar layer on the fiber surface improves the wettability and the affinity of the fiber surface for water and water-soluble dye molecules. After reaction with the functional groups, which are introduced by plasma treatment, dye molecules are fixed onto the fiber surface. Because plasmas do not interact with the inner part of the fiber, this technique may not greatly influence the mechanical properties of the treated fiber [12]. Great progress in improving dyeability of PP nonwoven webs had been made by the Textiles and Nonwovens development Center (TANDEC), University of Tennessee at Knoxville.

6.6. OTHER PROPERTIES OF PP

In general, PP fiber has excellent chemical resistance to acids and alkalis, high abrasion resistance and resistance to insects and pests. PP fiber is also easy to process and inexpensive compared to other synthetic fibers. Its low moisture absorption helps aid the quick transport of moisture.

6.7 DISADVANTAGES OF PP FIBERS

The main drawbacks of PP fibers are listed below:

- Low melting temperature which prevents it from being ironed like cotton, wool, nylon etc.,
- Hard to be dyed after manufacturing, except after substantial treatment and modification,
- High crystallinity and poor thermal conductivity leads to limited texturizability. [Drawn polypropylene requires a contact time of 2 seconds in the heater compared to PET (POY) which requires only 0.4 seconds]
- Poor UV and thermal stability which requires addition of expensive UV stabilizers and antioxidants to overcome this problem,
- Poor resilience compared to PET and Nylon,
- Creeping due to its low Tg(-15 to -20°C),
- Poor adhesion to glues and latex, and
- Flammable which melts and burns like wax.

Note: PP fiber has many useful textile properties; however, one key disadvantage is that it is flammable. Topical FR treatments have serious deficiencies, such as high add-on and limited durability. Dr. David Buszard [13] (FMC) introduced Reoflam FG-372, a new phosphorus-bromine based melt-processable flame retardant, stable at processing temperatures up to 230°C. It acts as a plasticier during fibre spinning, because of a similar melting temperature. An add-on level of 3% to 8% is required to meet the majority of textile flammability requirements. PP fibers containing Reoflam FG-372 are already being used in automative carpeting, where good light stability is also of importance.

7. APPLICATIONS

Because of its superior performance characteristics and comparatively low-cost, PP fiber finds extensive use in the nonwovens industry. PP is a very important fiber in nonwoven processing and dominates in many nonwoven markets. The main application areas include: nonwoven fabrics (refer to Table 3), particularly absorbent product coverstock markets, home furnishings and automotive markets.

Table 3: Application of Polypropylene Nonwoven fabrics.

Application	Fiber Grade	Industry
Cigarette Filter	Staple fiber 3 denier	Cigarette
Technical filters	Staple fiber 5 dsenier, needle punched nonwoven	Wet filteration, excellent, chemical resistance, used in water, milk, bear, paints, coatings, petrochemicals, Pharmaceuticals, filtration
PP woven socks	PP film fiber, with 10-15% LDPE to reduce fibrillation and cost	Fertilizers, flour, wheat, sugar, cement
Ropes and Twines	PP film and fiber	Agriculture
PP bale warp	Spun Bonded PP	Synthetic fibers
PP tapes	High modulus PP obtained by increasing draw ratio	Construction material like asphalt and concrete
PP construction / industry fabrics	Filling grade and staple fiber	Construction materials like asphalt and concrete
Substrate fabrics	Nonwoven needle punched 3-4 denier staple fibers	Furniture fabrics as backing material for visual furniture fabrics, it serves as reinforcement. Also used for wall covering, luggage, table-clothes, tarpaulins, and automobile
Outdoor Applications	Heavy deniers containing stabilizers, UV absorber, etc	Sports
Non-electric fuses for initiating explosives	PP slit film tapes	Mining industry
Medical/Surgical disposable fabric	PP staple fiber nonwovens, Face masks	Hospital

Below are some major olefin fiber uses:

7.1 CARPET AND UPHOLSTERY

Since polypropylene became a commercially available fiber more than 40 years ago, it has historically been a fiber for carpet and upholstery. About 90% of all carpet backing and more than 25% of all carpet face fiber is polypropylene [14]. In 1997 almost 3.8 billion pounds - approximately 39 percent of all fibers shipped by domestic manufacturers - were delivered to U.S. and Canadian carpet mills. Roughly 1.6 billion pounds of these shipments, 42 percent, were polypropylene filament and staple, representing more than 61 percent of all polypropylene shipments [15]. Table 4 details the growth of polypropylene filament staple distribution since 1993. In 1998, 44% polypropylene filament shipments were used as carpet-face fibers, with slightly more than half this amount, 514 million pounds or 24 percent of all filament shipments, were consumed in backing materials.

Table 4: Polypropylene Staple Fiber Shipments (millions of pounds)

	1993	1994	1995	1996	1997	1998
Carpet-face yarns	579.6	722.3	820.8	891.4	925.6	935
Carpet-backing yarns	454	485.6	405.7	478.2	488.2	514
Broadwoven	419.9	446.2	448	231.1	235.8	274
Narrow Wovens	19.6	21.3	21.8	15.8	16.5	18
Rope/Cordage/Fishline	113	114.1	121.6	118	111.4	130
Other	45.4	48.7	61.8	197.8	239	240
Total	1,631.5	1,838.2	1,879.7	1,932.3	2,016.5	2,111

Source: Fiber Economics Bureau and Author's Estimates

Polypropylene BCF (bulked continuous filament) yarns now account for almost 1 billion lbs/yr of the face fiber used in carpets and rugs in the U.S. Carpet mills that have back-integrated into fiber production make most of the BCF yarns used in the U.S. carpet industry. In 1998, the relatively low prices for polypropylene resins were a major factor in increased earnings for the major U.S. carpet and rug producers.

7.2 ABSORBENT PRODUCTS (Diapers)

Absorbent products are very important in the nonwovens business. Of the absorbent product applications, the baby diaper area is the largest volume user, however, applications in adult incontinence currently show the highest growth in recent years.

The major structural components of current diapers are[16].

- Top sheet (coverstock).
- Acquisition and/or transport or distribution layer.
- Absorbent core.
- Backsheet.

Secondary component materials are:

- Barrier leg cuffs.
- Elastomeric materials.
- Hot melt glues.

Current nonwoven materials used in topsheet applications include spunbonded polypropylene (usually produced on a multibeam system), SMS (spunbond/melt blown/spunbond) polypropylene composites and carded polypropylene thermal bonds. In some applications, thermally bonded bicomponent structures are being used.

Polypropylene spunbonded webs, treated to render them hydrophilic (or partially treated to make them hydrophilic in zones) have proved popular materials for coverstock applications, but they have not

always been rated as soft as other materials, i.e., staple fiber-based thermally bonded polypropylene.

However, recent developments in polymer technology with the availability of metallocene polypropylene would appear to provide a route to improve the resultant web softness. Alternative web-forming technologies, (such as those of Ason Engineering, Ft. Lauderdale, FL and Kobe, Tokyo, Japan) with the capability to produce bicomponent and microdenier webs, can now provide materials with better web formation, better softness and improved strength, allowing a reduction in web weight and consequently the possibility of a reduction in cost.

7.3. AUTOMOTIVE PRODUCTS

The nonwovens business in South America has continued to expand in more and more automotive product segments despite an automotive industry crisis [16]. The past year saw only 1.6 million units produced, a 24% drop from 1997. Sales during the year fell 21% and exports dropped 7.7%, from 416,000 to 384,000 units. Imports were another story, with new car imports growing 13.8%, from 303,000 to 345,000 in numbers of units. The negative trends in 1998 can largely be attributed to a combination of economic problems, increased unemployment levels, higher interest rates and tributary charges.

Principal polypropylene applications for nonwovens in automobiles are interior fabrics used in or on kick panel, package shelf, seat construction, truck liners, load decks, cabin air filters etc [18].

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DEVELOPMENT OF METALLOCENE BASED POLYPROPYLENE

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1. INTRODUCTION

In past decades, the use of polypropylene, has dominated in the production of melt blown and spunbonded nonwovens. The main reasons for the growing use of PP in polymer-laid nonwovens are that the raw materials are relatively inexpensive and available throughout the world, and PP resins can offer a relatively attractive cost combined with good value and ease of use when compared to conventional resins, such as polyester and polyamides. Continuing advances in PP fiber grade resins are strengthening the olefins price / properties ratio, which make them more suitable for polymer-laid nonwovens applications.

Polypropylene resins have been produced from Ziegler-Natta catalysts for over 30 years.

The drive for technology evolution has been the industry's desire to continuously improve control of the molecular architecture that leads to improved polymer performance.

In 1990's, the introduction of single site catalyst for making superior polyolefin resins set another technological trend, marked with Metallocene Catalysts having a precise control over molecular architecture for highly tailored polymers; improved processing; and properties for all polyolefins. This technology has been developed and designed for nonwoven applications [1]. The manufacturer may be able to take properties and very low extractables. Advantage of the higher barrier properties is to reduce basis weight or increase line speed. Because this material is so clean, the nonwoven manufacturer may be able to extend the intervals between die changes and process clean-ups. The absence of peroxide in

this product leads to reduced viscosity variations and more consistent extrusion performance. Reduced process air rates are possible with this material, which can reduce energy costs. Due to these advantages, this innovative new melt blown material is expected to gain rapid acceptance in the nonwovens industry.

2. ADVANTAGES OF METALLOCENE PP

Metallocene catalysts offer unique advantages versus conventional catalysts. They allow producing consistent, controllable molecular structures that can be designed to:

- Improve toughness
- Provide excellent impact resistance
- Reduce haze
- Provide excellent organoleptics (low off-taste and odor)
- Allow tailoring of processing characteristics to fit the conversion process
- It allows control the molecular structure of polyolefines.
- It enables to virtually eliminate non-targeted molecular weight species in resins
- It allows incorporation of co-monomers and ter-monomers with precision.
- It offers a greater control of molecular weight distribution (MWD).
- It leaves a small amount of catalyst residue in the finished product.

2.1 SPECIALTY OF METALLOCENE CATALYST

In PP manufacturing, the monomers are reacted using a catalyst. All catalysts have reactive sites enabling them to perform their function, i.e. linking individual molecules of monomers to form a polymeric chain. Conventional catalysts have many reactive sites located randomly on the surface of the catalysts. This produces different and varying polymers (See fig-1 below). The new catalyst system, which is known as single site catalyst, also has many reactive sites, but all sites are identical. This in turn gives identical polymers and does away variability of polymers.
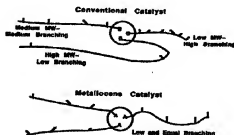

Fig. 1: Comparison of two types of catalysts [2]

3. METALLOCENE BASED PP NONWOVENS

Metallocene based PP resins for nonwovens and fiber applications can help to produce polymers with very low catalyst residues and very high purity. The polymer modification process, called controlled

rheology, enables us to tailor the resin for the specific need of nonwovens applications. Advantages of the fiber grade metallocene based PP resin in spunbonding and melt blowing over the conventional resin:

- It produces finer denier fibers than conventional resins.
- The optimum bonding temperatures are lower because of the lower melting point
- Excellent spinning continuity or fewer breaks in spinning.
- Spinning can be carried out at higher draw force.
- Substantial reduction in volatile deposits.
- Available in broader MFR range, especially helpful for melt blowing.
- Key features of Metallocene Polymers

The primary feature that makes metallocene-catalyzed polymers preferable to conventional polymers is structural uniformity, which eliminates very low and high molecular weight polymer components present with conventional catalysts (Fig.2).
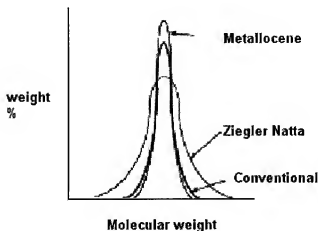

Fig. 2: Showing molecular weight distribution for various PP [3]

Table -1 Comparison of Metallocene PP with Conventional PP

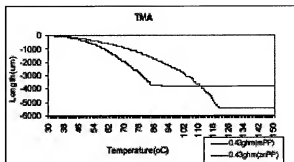| Product Attribute	Metallocene	Conventional PP
Melting Point (°C)	148	162
Flexural Modulus (MPa)	1380	1360
MWD (Mw/Mn)	2.0	3.5 / (2.8) *
Recoverable Compliance	0.4	3.5 / (0.9) *

Fig. 3: Thermo mechanical analysis (TMA) of filaments from different PP [4]

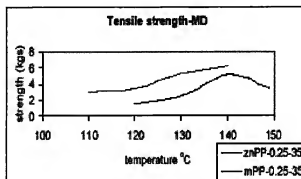*'mPP' means Metallocene PP,*
'znPP' means Conventional PP

Fig. 4: Tensile strength comparison of filaments from different PP [4]

4. APPLICATIONS

Presently, the metallocene based polyolefin polymers are produced by many companies in the world, but among those, BASF, Germany, and ExxonMobile Chemical Co., USA are the main producers of metallocene based PP. Exxon began development of *Escorene* Polypropylene grades used for nonwovens in 1960, and introduced Achieve[TM] propylene polymers based on *Exxpol* catalyst technology in 1995. This brought in overall property improvements versus conventional polypropylene yielding finer and stronger fibers at a lower production cost. Applications of Metallocene Polypropylene:

- Hygiene: diapers, disposals
- Medical: operation gowns and covers
- Filtration: air purification systems
- Household: mattress covers, upholstery, disposable products
- Wipes: wet wipes.
- Geotextiles

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Crystalline Structures

In addition, polymerized neighboring chains are held together by weak secondary (intermolecular) bonds known as van der Waals forces, as described in Module 2. As the chains grow during polymerization, they intermingle in a random pattern that will lead to an amorphous (disorderly) structure. Bear in mind that the growth of chains is three dimensional and not simply flat, as normally diagrammed. Visualize a bowl of cooked spaghetti with its uneven strands entangled; that gives a good idea of the arrangement of an amorphous polymer structure.

Actually, polymers are semicrystalline in varying degrees, with the amorphous structured polymers having only slight regularity, while other polymers may have a high degree of crystallinity (Figure 6-7). Metals achieve crystallinity due to the uniform nature of the unit cells of their space lattices. Crystallinity in polymers can alter strength and toughness. The twisting, coiling, and branching of polymer chains causes disorder, and amorphous regions develop in polymers as they solidify. Chain configuration and rate of cooling affect the orderliness. Slow cooling allows chains to move into alignment. While metals are normally fully crystalline, the degree of crystallinity in polymers can range from mostly amorphous to mostly crystalline. Mostly amorphous polymers will be less dense than mostly crystalline polymers because the chains pack closely together.

Molecular motion of short polymer chain segments and polymer branches cause amorphous polymers to be stiff, hard, and brittle at room temperatures. Increases in temperature cause greater molecular motion through thermal mixing of the atoms and molecules. This causes an increase in the volume of the material. The thermal mixing from higher temperatures also increases the spacing between molecular segments and permits increased flow of the materials. A discussion of glass transition later in this module deals further with the concept of molecular motion and flow in polymers.

The degree of crystallinity is determined by structural regularity, compactness, and amount of flexibility, which allows packing of chains. Reduction of random chain lengths provides regularity. Stronger secondary forces allow greater compacting. Liquid-crystal polymers (LCPS) develop highly oriented (rod-like) molecules for increased directional strength [Figure 6-7(d)]. Other chemical factors affect crystallinity, including configuration and tacticity [see Figure 6-3(e)-(g)]. See the references at the end of the module for more information.

Polyethylene serves as a good example of a polymer capable of a high degree of crystallinity because (1) the linear structure of the chains is conducive to packing, and (2) its molecular pattern is flexible, which provides easy packing even though it has weaker secondary bonding. Secondary bonds (van der Waals forces) normally promote crystallinity. Polyethylene (PE) has the potential for a wide range of properties because of technology's ability to control its molecular weight and crystallinity. Low-density polyethylene (LDPE) has a molecular weight below 10,000, while ultrahigh-density polyethylene (UHMWPE) has molecular weights much above 1.0×10^6 [see Figure 6-8(a)].

Crystallinity of polymers is also achieved through processes such as extrusion and drawing. Oriented polymer fibers are obtained by drawing an amorphous polymer through a die, which improves their strengths or orientation in the direction of drawing [see Figure 6-8(b)]. This concept can be illustrated by stretching a polyethylene sandwich bag. The method of manufacturing orients the polymers in one direction. By pulling on the bag in perpendicular directions it is possible to notice the greater resistance from the oriented direction; also, as the bag is stretched, it becomes stronger due to further orientation.

The cooling rate and processing during cooling affect the crystal patterns. Spherulites form, in which

nuclei generate a spherical pattern that grows until several spheralites melt at boundaries, as a result of supercooling. When large spherulites are allowed to grow, weakness results. Heat treatment of polymers can change their crystal structure; for example, the annealing processes reheat the polymer for a specified time to permit crystal thickening. In Figure 6-9, electron micrographs show polyethylene in the amorphous state, then as a single linear crystal, and then as an annealed crystal.